

Auger-Photoelectron Coincidence Spectroscopy Study of the Dilute Pd/Ag(100) Surface Alloy

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Surface alloys are a class of bimetallic systems where the two metals intermix only in the first atomic layer. Some surface alloys occur between immiscible metals while others are in a kinetically limited metastable state. Typically, surface alloys occur at very low impurity concentrations ($< 10\%$ ML) and their electronic structure differs significantly from that of their parent materials. APECS is ideally suited for studying the electronic properties of these systems, as it is very surface sensitive, it is element specific, and the background from the host materials can be eliminated.

In this project we have examined the line shape of the Pd $M_{45}VV$ and M_5VV Auger transition in coincidence with Pd $3d_{3/2}$ and $3d_{5/2}$ core photoelectrons, respectively, from the Pd/Ag(100) surface alloy system. The Pd $M_{45}VV$ Auger transition is known to have an anomalous line shape bulk PdAg alloy when the Pd concentration is 10% or less. **Figure 1** shows two singles Pd $M_{45}VV$ Auger spectra obtained from a thick Pd film (upper curve) and 0.1 ML Pd (lower curve) on the Ag(100) surface. The lower curve exhibits the anomalous line shape found for similar Pd concentrations in the bulk. The spectrum is characterized by features at 325 eV and 330 eV that are absent from both the bulk and atomic Pd spectra. In particular, it is unclear whether the 325 eV feature is associated with the M_4 or the M_5 line.

In **Figure 2** we present the coincidence M_5VV and M_4VV Auger spectra (solid circles with error bars) along with the simultaneously acquired singles spectra (dotted line) and a calculation of the M_4 and M_5 line shapes performed by Hedegard *et al.*[1]. Concentrating on the M_5 line, we find that the 325 eV feature, which is the most intense feature of the single spectrum, is indeed associated with the M_5VV Auger spectrum. Furthermore, the line shape of the coincidence spectrum is well described by the theoretical curve. According to this calculation, the 325 eV feature is associated with the presence of a virtual bound state on the Pd site that is formed by interaction of the d -levels of the isolated Pd atoms with the sp -continuum of the Ag host. The lower kinetic energy feature at 332 eV arises from hybridization between the Pd d -levels and the Ag d -band.

The lower frame of **Figure 2**, which shows the coincidence M_4VV spectrum, exhibits a more complicated line shape. This is in part because the spectrum contains a residual contribution from the M_5VV line owing to inelastically scattered Pd $3d_{5/2}$ photoelectrons occurring at the same kinetic energy as the primary $3d_{3/2}$ emission. However, even without subtracting this contribution, it is clear that the high kinetic energy features at 330 eV and 327.5 eV are the equivalent virtual bound state and hybridization features associated with the decay of the $3d_{3/2}$ level.

In summary, using APECS to isolate the overlapping components of the Pd $M_{45}VV$ Auger spectrum from the dilute Pd/Ag(100) surface alloy, we have unambiguously identified the origin of several anomalous features, which have caused controversy in the literature for many years.

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References: [1] P. Hedegard and B. Johansson, Phys. Rev. Lett. **52** (1984) 2168.

Anomalous Pd $M_{45}VV$ Lineshape
for dilute surface alloy

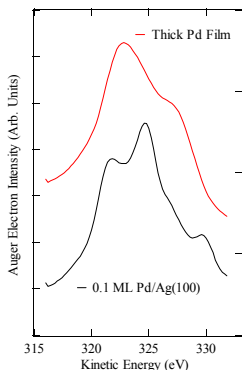


Figure 1

Coincidence Pd M_5VV and M_4VV Spectra
from Dilute Pd/Ag Surface Alloy

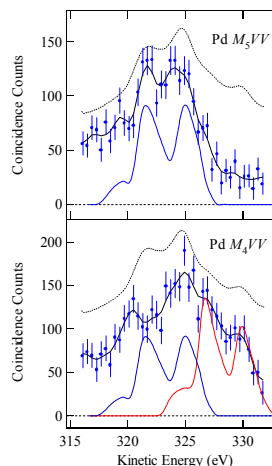


Figure 2